CLAIMS

We claim:

1. A process to polymerize one or more olefin(s) in the presence of a catalyst composition comprising combining a solid or a slurry comprising one or more bulky ligand metallocene catalyst compounds, a support and or one or more activator(s) with a solution comprising one or more phenoxide catalyst compounds, and thereafter, introducing the combination into a polymerization reactor.

2. The process of claim 1 wherein the slurry comprises a supported alumoxane and or a supported modified alumoxane.

3. The process of clam 1 wherein the slurry is formed by combining a supported activator with a liquid and a bulky ligand metallocene catalyst compound.

4. The process of claim 1 wherein the slurry comprises a supported catalyst system comprising a bulky ligand metallocene catalyst compound, an activator and a support.

5. The process of claim 4 wherein the supported catalyst system is prepared by combining the bulky ligand metallocene catalyst compound, the activator and the support in a solvent and thereafter removing the solvent.

6. The process of claim 4 wherein the supported catalyst system is prepared by combining the catalyst compound, the activator and the support in a solvent and thereafter spray drying the mixture.

7. The process of claim 1 wherein after combination at least 50% of the catalyst compounds are deposited in or on the support.

8. The process of claim 1 wherein after combination at least 80% of the catalyst compounds are deposited in or on the support.

9. The process of claim 1 wherein the activator comprises a non-coordinating anion or an ionizing compound.

10. The process of claim 1 wherein the activator comprises one or more from the group consisting of: trimethylammonium tetraphenylborate, triethylammonium tetraphenylborate, tripropylammonium tetraphenylborate, tri(n-butyl)ammonium tetraphenylborate, tri(t-butyl)ammonium tetraphenylborate, N,N-dimethylanilinium tetraphenylborate; N,N-diethylanilinium tetraphenylborate, N,N-dimethyl-(2,4,6-trimethylanilinium) tetraphenylborate, trimethylammonium tetrakis (pentafluorophenyl)borate, triethylammonium tetrakis(pentafluorophenyl)borate, tripropylammonium tetrakis(pentafluorophenyl)borate, tri(n-butyl)ammonium tetrakis(pentafluorophenyl)borate, tri(sec-butyl)ammonium tetrakis (pentafluorophenyl) borate, N,N-dimethylanilinium tetrakis(pentafluorophenyl) borate, N,N-diethylanilinium tetrakis(pentafluorophenyl) borate, N,N-dimethyl-(2,4,6-trimethylanilinium) tetrakis(pentafluorophenyl) borate, trimethylammonium tetrakis-(2,3,4,6-tetrafluorophenylborate triethylammonium tetrakis-(2,3,4,6-tetrafluorophenyl) borate, tripropylammonium tetrakis-(2,3,4,6-tetrafluorophenyl) borate; tri(n-butyl)ammonium tetrakis-(2,3,4,6-tetrafluoro-phenyl) borate, dimethyl (t-butyl)ammonium tetrakis-(2,3,4,6-tetrafluorophenyl) borate, N,N-dimethylanilinium tetrakis-(2,3,4,6-tetrafluorophenyl) borate, N,N-

diethylanilinium tetrakis-(2,3,4,6-tetrafluoro-phenyl) borate, and N,N-dimethyl-(2,4,6-trimethylanilinium)tetrakis-(2,3,4,6-tetrafluorophenyl) borate, di-(i-propyl)ammonium tetrakis(pentafluorophenyl) borate, and dicyclohexylammonium tetrakis(pentafluorophenyl) borate, triphenyl-phosphonium tetrakis(pentafluorophenyl) borate, tri(o-tolyl)phosphonium tetrakis(pentafluorophenyl) borate, and tri(2,6-dimethylphenyl)phosphonium tetrakis(pentafluorophenyl) borate.

11. The process of claim 1 wherein the bulky ligand metallocene catalyst compound is represented by the formula:

$$L^AL^BMQ_n \quad (I)$$

or $$L^AAL^BMQ_n \quad (II)$$

or $$L^CAJMQ_n \quad (III)$$

where M is a Group 3 to 12 metal or a lanthanide or actinide element,
L^A, L^B and L^C are each independently bulky ligands selected from the group consisting of cyclopentadienyl ligands, cyclopentaphenanthreneyl ligands, indenyl ligands, benzindenyl ligands, fluorenyl ligands, octahydrofluorenyl ligands, cyclooctatetraendiyl ligands, cyclopentacyclododecene ligands, azenyl ligands, azulene ligands, pentalene ligands, phosphoyl ligands, phosphinimine, aminomethylphosphine ligands, pyrrolyl ligands, pyrozolyl ligands, carbazolyl ligands, borabenzene ligands, B-diketiminate ligands, fullerenes and hydrogenated versions thereof,
each Q is independently a leaving group,
A is a bridging group containing at least one Group 13 to 16 atom,
J is a heteroatom ancillary ligand, and
n is 0, 1 or 2,
in formula III, M is bound to L^C and J, and A is bound to L^C and J.

12. The method of claim 1 wherein the bulky ligand metallocene catalyst compound is represented by the formula:

$$L^DMQ_2(YZ)X_n$$

where M is a Group 3 to 16 metal,

L^D is a bulky ligand that is bonded to M selected from the group consisting of selected from the group consisting of cyclopentadienyl ligands, cyclopentaphenanthreneyl ligands, indenyl ligands, benzindenyl ligands, fluorenyl ligands, octahydrofluorenyl ligands, cyclooctatetraendiyl ligands, cyclopentacyclododecene ligands, azenyl ligands, azulene ligands, pentalene ligands, phosphoyl ligands, phosphinimine, aminomethylphosphine ligands, pyrrolyl ligands, pyrozolyl ligands, carbazolyl ligands, borabenzene ligands, B-diketiminate ligands, fullerenes and hydrogenated versions thereof,

each Q is independently bonded to M and $Q_2(YZ)$ forms a unicharged polydentate ligand; A or Q is a univalent anionic ligand also bonded to M;

X is a univalent anionic group when n is 2 or X is a divalent anionic group when n is 1; n is 1 or 2.

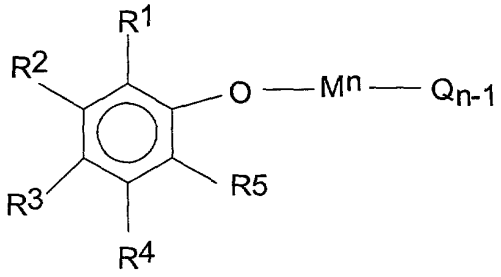
13. The method of claim 1 wherein the bulky ligand metallocene catalyst compound is represented by the formula:

$$((Z)XA_t(YJ))_qMQ_n$$

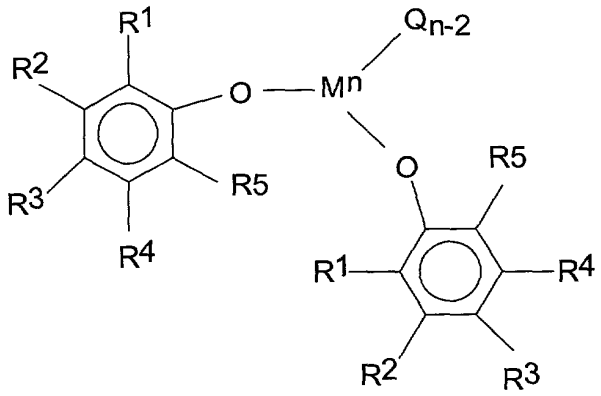
where M is a metal selected from Group 3 to 13 or lanthanide and actinide series of the Periodic Table of Elements; Q is bonded to M and each Q is a monovalent, bivalent, or trivalent anion; X and Y are bonded to M; one or more of X and Y are heteroatoms; Y is contained in a heterocyclic ring J, where J comprises from 2 to 50 non-hydrogen atoms, Z is bonded to X, where Z comprises 1 to 50 non-hydrogen

atoms; t is 0 or 1; when t is 1, A is a bridging group joined to at least one of X, Y or J, q is 1 or 2; n is an integer from 1 to 4.

14. The process of claim 1 wherein the phenoxide catalyst compound is represented by the formula:



or



wherein

R^1 is hydrogen or a C_4 to C_{100} group and may or may not also be bound to M, and at least one of R^2 to R^5 is a group containing a heteroatom, the rest of R^2 to R^5 are independently hydrogen or a C_1 to C_{100} group, and any of R^2 to R^5 also may or may not be bound to M,

O is oxygen,

M is a group 3 to group 10 transition metal or lanthanide metal,

n is the valence state of the metal M,

Q is an alkyl, halogen, benzyl, amide, carboxylate, carbamate, thiolate, hydride or alkoxide group, or a bond to an R group containing a heteroatom which may be any of R^1 to R^5.

15. The process of claim 1 wherein the polymerization reactor is a gas phase polymerization reactor.

16. The process of claim 1 wherein the polymerization reactor is a slurry phase polymerization reactor.

17. The process of claim 1 wherein the bulky ligand metallocene catalyst compound is selected from one of the group consisting of: bis(cyclopentadienyl)titanium dimethyl,

bis(cyclopentadienyl)titanium diphenyl,
bis(cyclopentadienyl)zirconium dimethyl,
bis(cyclopentadienyl)zirconium diphenyl, bis(cyclopentadienyl) hafnium methyl and diphenyl, bis(cyclopentadienyl)titanium di-neopentyl,
bis(cyclopentadienyl)zirconium di-neopentyl,
bis(cyclopentadienyl)titanium dibenzyl,
bis(cyclopentadienyl)zirconium dibenzyl, bis(cyclopentadienyl) vanadium dimethyl, bis(cyclopentadienyl)titanium methyl chloride, bis(cyclopentadienyl)titanium ethyl chloride, bis(cyclopentadienyl) titanium phenyl chloride, bis(cyclopentadienyl)zirconium methyl chloride, bis (cyclopentadienyl)zirconium ethyl chloride, bis(cyclopentadienyl)zirconium phenyl chloride,
bis(cyclopentadienyl)titanium methyl bromide,
cyclopentadienyl titanium trimethyl, cyclopentadienyl zirconium triphenyl,
cyclopentadienyl zirconium trineopentyl, cyclopentadienyl zirconium trimethyl,
cyclopentadienyl hafnium triphenyl, cyclopentadienyl hafnium trineopentyl,
cyclopentadienyl hafnium trimethyl,pentamethylcyclopentadienyl titanium trichloride, pentaethylcyclopentadienyl titanium trichloride; bis(indenyl)titanium diphenyl or dichloride,
bis(methylcyclopentadienyl)titanium diphenyl or dihalide, bis(1,2-dimethylcyclopentadienyl)titanium diphenyl or dichloride,
bis(1,2-diethylcyclopentadienyl)titanium diphenyl or dichloride,
bis(pentamethylcyclopentadienyl) titanium diphenyl or dichloride; dimethyl silyldicyclopentadienyl titanium diphenyl or dichloride,
methyl phosphine dicyclopentadienyl titanium diphenyl or dichloride,

methylenedicyclopentadienyl titanium diphenyl or dichloride,
isopropyl(cyclopentadienyl)(fluorenyl)zirconium dichloride,
isopropyl(cyclopentadienyl)(octahydrofluorenyl)zirconium dichloride,
diisopropylmethylene(cyclopentadienyl)(fluorenyl)zirconium dichloride,
diisobutylmethylene(cyclopentadienyl)(fluorenyl) zirconium dichlorie,
ditertbutylmethylene(cyclopentadienyl)(fluorenyl)zirconium dichloride,
cyclohexylidene(cyclopentadienyl)(fluorenyl)zirconium dichloride,
diisopropylmethylene(2,5-dimethylcyclopentadienyl)(fluorenyl)zirconium dichloride,
isopropyl(cyclopentadienyl)(fluorenyl)hafniium dichloride,
diphenylmethylene(cyclopentadienyl)(fluorenyl)hafnium dichloride,
diisopropylmethylene(cyclopentadienyl)(fluorenyl)hafium dichloride,
diisobutylmethylene(cyclopentadienyl)(fluorenyl)hafnium dichloride,
ditertbutylmethylene(cyclopentadienyl)(fluorenyl)hafnium dichloride,
cyclohexylidene(cyclopentadienyl)(fluorenyl)hafnium dichloride,
diisopropylmethylene(2,5-dimethylcyclopentadienyl) (fluorenyl)-hafnium dichloride, isopropyl(cyclopentadienyl)(fluorenyl)titanium dichloride,
diphenylmethylene(cyclopentadienyl)(fluorenyl)titanium dichloride,
diisopropylmethylene(cyclopentadienyl)(fluorenyl)titanium dichloride,
diisobutylmethylene(cyclopentadienyl)(fluorenyl)titanium dichloride,

ditertbutylmethylene(cyclopentadienyl)(fluorenyl)titanium dichloride,
cyclohexylidene(cyclopentadienyl)(fluorenyl)titanium dichloride, diisopropylmethylene(2,5 dimethylcyclopentadienyl fluorenyl)titanium dichloride, racemic-ethylene bis(1-indenyl)zirconium (W) dichloride,
racemic-ethylene bis (4,5,6,7-tetrahydro-1-indenyl) zirconium (IV) dichloride,
racemic-dimethylsilyl bis (1-indenyl) zirconium (IV) dichloride,
racemic-dimethylsilyl bis (4,5,6,7-tetrahydro-1-indenyl) zirconium (IV)
dichloride, racemic-1,1,2,2-tetramethylsilanylene bis (1-indenyl) zirconium (IV) dichloride, racemic-1,1,2,2-tetramethylsilanylene bis (4,5,6,7-tetrahydro-1-indenyl) zirconium (IV) dichloride, ethylidene (1-indenyl tetramethylcyclopentadienyl) zirconium (IV) dichloride, racemic-dimethylsilyl bis (2-methyl-4-t-butyl-1-cyclopentadienyl) zirconium (IV) dichloride,
racemic-ethylene bis (1-indenyl) hafnimn (IV) dichloride, racemic-ethylene bis (4,5,6,7-tetrahydro-1-indenyl) hafiium (IV) dichloride, racemic-dimethylsilyl bis (1-indenyl) hafaium (IV) dichloride, racemic-dimethylsilyl bis (4,5,6,7-tetrahydro-1-indenyl) hafnium (IV) dichloride, racemic-1,1,2,2-tetramethylsilanylene bis (1-indenyl) hafnium (IV) dichloride, racemic-1,1,2,2-tetramethylsilanylene bis (4,5,6,7-tetrahydro-1-indenyl) hafnium (IV), dichloride, ethylidene (1-indenyl-2,3,4,5-tetramethyl-1-cyclopentadienyl) hafnium (IV) dichloride, racemic-ethylene bis (1-indenyl) titanium (IV) dichloride, racemic-ethylene bis (4,5,6,7-tetrahydro-1-indenyl) titanium (IV) dichloride, racemic-dimethylsilyl bis (1-indenyl) titanium (IV) dichloride,

racemic-dimethylsilyl bis (4,5,6,7-tetrahydro-1-indenyl) titanium (IV)dichloride,
racemic-1,1,2,2-tetramethylsilanylene bis (1-indenyl) titanium (IV) dichloride
racemic-1,1,2,2-tetramethylsilanylene bis (4,5,6,7-tetrahydro-1-indenyl) titanium (IV) dichloride, and ethylidene (1-indenyl-2,3,4,5-tetramethyl-1-cyclopentadienyl) titanium (IV) dichloride.

18. The process of claim 1 wherein the phenoxide catalyst compound is selected from one of the group consisting of:
(*N*-methyl-3,5-di-*t*-butylsalicylimino)zirconium(IV) dibenzyl;
bis(*N*-ethyl-3,5-di-*t*-butylsalicylimino)zirconium(IV) dibenzyl;
bis(*N*-*iso*-propyl-3,5-di-*t*-butylsalicylimino)zirconium(IV) dibenzyl;
bis(*N*-*t*-butyl-3,5-di-*t*-butylsalicylimino)zirconium(IV) dibenzyl;
bis(*N*-benzyl-3,5-di-*t*-butylsalicylimino)zirconium(IV) dibenzyl;
bis(*N*-hexyl-3,5-di-*t*-butylsalicylimino)zirconium(IV) dibenzyl;
bis(*N*-phenyl-3,5-di-*t*-butylsalicylimino)zirconium(IV) dibenzyl;
bis(*N*-methyl-3,5-di-*t*-butylsalicylimino)zirconium(IV) dibenzyl;
bis(*N*-benzyl-3,5-di-*t*-butylsalicylimino)zirconium(IV) dichloride;
bis(*N*-benzyl-3,5-di-*t*-butylsalicylimino)zirconium(IV) dipivalate;
bis(*N*-benzyl-3,5-di-*t*-butylsalicylimino)titanium(IV) dipivalate;
bis(*N*-benzyl-3,5-di-*t*-butylsalicylimino)zirconium(IV) di(bis(dimethylamide));
bis(*N*-*iso*-propyl-3,5-di-*t*-amylsalicylimino)zirconium(IV) dibenzyl;
bis(*N*-*iso*-propyl-3,5-di-*t*-octylsalicylimino)zirconium(IV) dibenzyl;
bis(*N*-*iso*-propyl-3,5-di-(1',1'-dimethylbenzyl)salicylimino)zirconium(IV) dibenzyl;
bis(*N*-*iso*-propyl-3,5-di-(1',1'-dimethylbenzyl)salicylimino)titanium(IV) dibenzyl;

bis(*N-iso*-propyl-3,5-di-(1',1'-dimethylbenzyl)salicylimino)hafnium(IV) dibenzyl;

bis(*N-iso*-butyl-3,5-di-(1',1'-dimethylbenzyl)salicylimino)zirconium(IV) dibenzyl;

bis(*N-iso*-butyl-3,5-di-(1',1'-dimethylbenzyl)salicylimino)zirconium(IV) dichloride;

bis(*N*-hexyl-3,5-di-(1',1'-dimethylbenzyl)salicylimino)zirconium(IV) dibenzyl;

bis(*N*-phenyl-3,5-di-(1',1'-dimethylbenzyl)salicylimino)zirconium(IV) dibenzyl;

bis(*N-iso*-propyl-3,5-di-(1'-methylcyclohexyl)lsalicylimino)zirconium(IV) dibenzyl;

bis(*N*-benzyl-3-*t*-butylsalicylimino)zirconium(IV) dibenzyl;

bis(*N*-benzyl-3-triphenylmethylsalicylimino)zirconium(IV) dibenzyl;

bis(*N-iso*-propyl-3,5-di-trimethylsilylsalicylimino)zirconium(IV) dibenzyl;

bis(*N-iso*-propyl-3-(phenyl)salicylimino)zirconium(IV) dibenzyl;

bis(*N*-benzyl-3-(2',6'-di-*iso*-propylphenyl)salicylimino)zirconium(IV) dibenzyl;

bis(*N*-benzyl-3-(2',6'-di-phenylphenyl)salicylimino)zirconium(IV) dibenzyl;

bis(*N*-benzyl-3-*t*-butyl-5-methoxysalicylimino)zirconium(IV) dibenzyl;

bis(2-(2H-benzotriazol-2-yl)-4,6-di-*t*-amylphenoxide)zirconium(IV) dibenzyl;

bis(2-(2H-benzotriazol-2-yl)-4,6-di-*t*-amylphenoxide)zirconium(IV) dichloride;

bis(2-(2H-benzotriazol-2-yl)-4,6-di-*t*-amylphenoxide)zirconium(IV) di(bis(dimethylamide)); bis(2-(2H-benzotriazol-2-yl)-4,6-di-(1',1'-dimethylbenzyl)phenoxide)zirconium(IV) dibenzyl; bis(2-(2H-benzotriazol-2-yl)-4,6-di-*t*-amylphenoxide)titanium(IV) dibenzyl; bis(2-(2H-benzotriazol-2-yl)-4,6-di-(1',1'-

dimethylbenzyl)phenoxide)titanium(IV) dibenzyl; bis(2-(2H-benzotriazol-2-yl)-4,6-di-(1',1'-dimethylbenzyl)phenoxide)titanium(IV) dichloride; bis(2-(2H-benzotriazol-2-yl)-4,6-di-(1',1'-dimethylbenzyl)phenoxide)hafnium(IV) dibenzyl; (*N*-phenyl-3,5-di-(1',1'-dimethylbenzyl)salicylimino)zirconium(IV) tribenzyl; (*N*-(2',6'-di-*iso*-propylphenyl)-3,5-di-(1',1'-dimethylbenzyl)salicylimino)zirconium(IV) tribenzyl; (*N*-(2',6'-di-*iso*-propylphenyl)-3,5-di-(1',1'-dimethylbenzyl)salicylimino)titanium(IV) tribenzyl; and (*N*-(2',6'-di-*iso*-propylphenyl)-3,5-di-(1',1'-dimethylbenzyl) salicylimino)zirconium(IV) trichloride.

19. The process of claim 1 wherein the bulky ligand metallocene catalyst compound comprises bis(2,4 methylbutylcyclpentadienyl) zirconium dihalide and the phenoxide catalyst compound comprises bis(N-iso-butyl-3-t-butylsalicyclimino)zirconium (IV)dibenzyl.

20. The process of claim 1 wherein prior to combination the solution comprises less than 1 weight percent activator.

21. The method of claim 19 wherein the activator comprises supported alumoxane.

22. The method of claim 1 wherein the slurry comprises mineral oil and has a viscosity of about 130 to about 2000 cP at 20°C.

23. The method of claim 1 wherein the combination of the solution and the slurry has a viscosity of about 130 to about 2000 cP at 20°C.

24. The method of claim 1 wherein the solution does not comprise mineral oil and comprises up to 20 weight % of the combination of the solution and the slurry.

25. The method of claim 1 wherein the solution comprises mineral oil and comprises up to 90 weight % of the combination of the solution and the slurry.

26. The method of claim 1 wherein the solution and the slurry are mixed for up to about 120 minutes prior to being introduced into the reactor.

27. The method of claim 1 wherein the solution and the slurry are mixed for about 1 minute to about 60 minutes prior to being introduced into the reactor.

28. A polymer produced by the process of claim 1.

29. A composition comprising a polymer of ethylene wherein the polymer has a density of 0.910 to 0.930 g/cc, a melt index of 0.3-2.0 dg/min, and a 15-35 μm thick film of the polymer has a 45° gloss of 60 or more, a haze of 7% or less, a dart impact of 600 g or more.

30. The composition of claim 29 wherein the film also has a transverse direction tensile strength of 30 MPa or more.

31. The composition of claim 29 wherein the film also has a machine direction tensil strength of 30 MPa or more.

32. The composition of claim 29 wherein the film has a machine direction modulus of 150 MPa or more.

33. The composition of claim 29 wherein the film has a transverse direction modulus of 150 MPa or more.

34. The composition of claim 29 wherein the film has a machine direction Elmendorf tear of 180 g/mil or more.

35. The composition of claim 29 wherein the film has a transverse direction Elmendorf tear of 300 g/mil or more.

36. The composition of claim 29 wherein the film also has:
a transverse direction tensile strength of 30 MPa or more,
a machine direction tensil strength of 30 MPa or more,
a machine direction modulus of 150 MPa or more,
a transverse direction modulus of 150 MPa or more,
a machine direction Elmendorf tear of 180 g/mil or more, and
a transverse direction Elmendorf tear of 300 g/mil or more.